

University of Groningen

## Liquefaction of humins from C6-sugar conversions using heterogeneous catalysts

Wang, Yuehu

**IMPORTANT NOTE:** You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*

2017

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Wang, Y. (2017). *Liquefaction of humins from C6-sugar conversions using heterogeneous catalysts*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

# **Liquefaction of Humins from C<sub>6</sub>-Sugar Conversions using Heterogeneous Catalysts**

**YUEHU  
WANG**

# **Liquefaction of Humins from C<sub>6</sub>-Sugar Conversions using Heterogeneous Catalysts**

## **PhD thesis**

to obtain the degree of PhD at the  
University of Groningen  
on the authority of the  
Rector Magnificus Prof. E. Sterken  
and in accordance with  
the decision by the College of Deans.

This thesis will be defended in public on

Friday 17 March 2017 at 16.15 hours

by

**Yuehu Wang**

born on 18 April 1980  
in Guizhou, China

This work was financially supported by the Dutch CatchBio Program, part of the Smart Mix program of the Netherlands ministry of Economic Affairs and the Netherlands ministry of Education, Culture and Science.

Layout and cover design:  Lovebird design.  
[www.lovebird-design.com](http://www.lovebird-design.com)

Printed by: Eikon+

ISBN: 978-90-367-9539-5

## Supervisor

Prof. H.J. Heeres

## Assessment committee

Prof. A.A. Broekhuis

Prof. F. Picchioni

Prof. K. Seshan

## TABLE OF CONTENTS

<b>1. Introduction</b>	<b>9</b>
1.1. The Biorefinery Concept	11
1.2. Platform Chemicals from Biomass	12
1.3. Biobased chemicals: 5-Hydroxymethylfurfural (HMF) and Levulinic Acid (LA)	15
1.3.1. General	15
1.3.2. Synthesis and production of HMF	15
1.3.2.1. Synthetic procedures	15
1.3.2.2. Commercial status HMF production	17
1.3.3. LA synthesis and production	18
1.3.3.1. Synthetic procedure for LA	18
1.3.3.2. Commercial status LA production	18
1.4. Humins: molecular structure	19
1.4.1. General features	19
1.4.2. Soil humins	20
1.4.3. Structural features of humins from sugar conversions	22
1.4.4. Structural models for HTC	23
1.4.5. Structural models for humins from acid catalysed sugar conversions	24
1.5. Valorisation of Humins	27
1.6. Scope and Outline of this Thesis	30
1.7. References	32
<b>2. Formation, Molecular Structure and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions</b>	<b>39</b>
2.1. Introduction	41
2.2. Results and Discussion	49
2.2.1. Preparation and purification of humin samples	49
2.2.2. Formation of humin by-products	50
2.2.3. Elemental composition of humin by-products	53
2.2.4. Morphology of humin by-products	54
2.2.5. Characterisation of liquid phase products	56
2.2.6. Molecular structure: Characterisation by IR and NMR spectroscopy and Pyrolysis/GC-MS	58
2.3. Conclusions	67
2.4. Experimental Section	69
2.5. References	71
2.6. Supporting information	74
<b>3. Exploratory catalyst screening studies on the liquefaction of humins from C<sub>6</sub> sugar biorefineries</b>	<b>77</b>
3.1. Introduction	79
3.2. Materials and Methods	82
3.3. Results and Discussion	87
3.3.1. Catalyst characterisation for the metal on carbon catalysts	87
3.3.2. Exploratory catalyst screening studies for noble metals on a carbon support	88
3.3.2.1. Product phases	88
3.3.2.2. Humin conversion	90

3.3.2.3.	Blank reactions.....	91
3.3.2.4.	Liquid phase composition. ....	92
3.3.2.5.	GC-MS-FID.....	92
3.3.2.6.	GC×GC analysis of the products .....	94
3.3.3.	Reaction pathways .....	98
3.3.4.	Systematic studies for Pt catalysts on various supports .....	101
3.3.4.1.	Catalyst Characterisation .....	101
3.3.4.2.	Catalyst screening studies for Pt on various inorganic supports .....	103
3.3.4.3.	Analysis of the liquid product phase .....	103
3.4.	Conclusions .....	106
3.5.	References .....	108
3.6.	Supporting information.....	112
<b>4.</b>	<b>Catalytic Liquefaction of Humin Substances from Sugar Biorefineries with Pt/C in 2-propanol .....</b>	<b>117</b>
4.1.	Introduction .....	119
4.2.	Materials and Methods.....	121
4.3.	Results and Discussion .....	126
4.3.1.	Benchmark experiments .....	126
4.3.2.	Systematic studies using Pt/C and IPA .....	136
4.3.2.1.	Humin conversion .....	136
4.3.2.2.	Liquid yield.....	141
4.3.2.3.	Alkylphenolics yield .....	141
4.4.	Conclusions .....	143
4.5.	References: .....	144
4.6.	Supplementary information .....	147
<b>5.</b>	<b>Catalytic hydrotreatment of Humins in Formic Acid/2-Propanol mixtures using supported Ru catalysts .....</b>	<b>151</b>
5.1.	Introduction .....	153
5.2.	Materials and methods.....	158
5.3.	Results and Discussion .....	163
5.3.1.	Screening experiments. ....	163
5.3.2.	Composition of the gas and liquid phase for catalytic hydrotreatments with Ru/C.....	166
5.3.2.1.	Gas phase composition.....	166
5.3.2.2.	Liquid phase composition for experiments with Ru/C.....	166
5.3.2.2.1.	Elemental composition of the humin oils .....	166
5.3.2.2.2.	Molecular composition of the humin oils .....	168
5.3.2.2.3.	Catalyst support effects.....	174
5.3.3.	Reaction pathways .....	175
5.4.	Conclusions .....	178
5.5.	References .....	178
5.6.	Supplementary information .....	182
<b>6.</b>	<b>Summary.....</b>	<b>187</b>
<b>7.</b>	<b>Samenvatting (Dutch Summary).....</b>	<b>191</b>
<b>8.</b>	<b>Acknowledgements .....</b>	<b>195</b>
<b>9.</b>	<b>List of Publications.....</b>	<b>198</b>